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3

ENVIRONMENTAL CONDITIONS

Radiative flux determines the conditions under which materials function and degrade. The effect of temperature on degradation rate must also be considered since heat is another form of energy which acts simultaneously on materials. The composition of the atmosphere, including the moisture component, affect radiative flux but moisture, in particular, and other atmospheric components initiate changes, often corrosive in exposed materials. Volcanoes, on eruption, produce gaseous and particulate pollutants. Winds contribute to the transportation of matter and thus to the residence time of pollutants in the atmosphere and to climate formation. Winds also affect temperature distribution in samples during exposure. Clouds produce precipitation but also absorb sun radiation and reflect or absorb re-radiated energy. Lightning produces energy utilized for chemical reactions in the atmosphere. All of these, due to general circulation and transport processes, contribute to the climatic or environmental conditions which affect exposed material and in which they must be designed to work. The following analysis outlines important features and relations of these environmental conditions.[1-12]

3.1 SOLAR RADIATIVE EMISSION

Outer space surrounding the Earth does not contain material particles; therefore the only form in which energy can be supplied to our planet is by radiation. Radiation is emitted by all matter having temperature higher than absolute zero. The energy of emitted radiation is described by Planck's Law:

$$E_\lambda = c_1[\lambda^5(\exp c_2/\lambda T) - 1] \qquad [1]$$

where
- E_λ amount of energy emitted at a specific wavelength, λ
- T absolute temperature
- c_1, c_2 constants.

The Stefan-Boltzmann Law:

$$E^* = \sigma T^4 \qquad [2]$$

where E^* total energy emitted by a body
σ the Stefan-Boltzmann constant
T absolute temperature

shows that the total energy emitted by a body depends on its temperature as does its wavelength of maximum emission, according to Wien's Law:

$$\lambda_{max} = 2897T \qquad [3]$$

where λ_{max} wavelength of maximum emission
T absolute temperature.

Rydberg's Law specifies the radiation wavelength:

$$1/\lambda = R[1/(n+a)^2 - 1/(m+b)^2] \qquad [4]$$

where λ radiation wavelength
n, m integers, m>n
a, b constants for particular series
R Rydberg constant.

According to this equation, each element is capable of emitting radiation at several specific lines restricted by the values of constants included in the equation. Solar radiation does not depend on just one element; rather, the spectrum of light emitted results from a combination of component spectra and their relative concentrations. Evidently, the radiative emission of the sun depends on the combination of elements involved in the energy generation process and on the temperature at which radiation occurs. This should then tell us that the radiative emission of the sun should be constant if both temperature and the concentration of elements involved are also constant.

The sun was formed 4.6 billions years ago and it is composed of 74% hydrogen and 25% helium by mass. The remaining 1% comprises elements, such as oxygen, carbon, silicon, iron, magnesium, and calcium. The sun emits energy generated by the thermonuclear fusion of hydrogen into helium at a temperature of around 1.5 million degrees K. This thermonuclear fusion process occurs in the core of the sun and energy is passed to the photosphere. The core contains more helium (65%) than hydrogen. Hydrogen is deficient because of its conversion in the thermonuclear fusion process. It is estimated that

the remaining hydrogen should last for another 4 billion years at the sun's recent level of luminosity.

The photosphere does not have a uniform temperature; it varies between 4000 and 8000 K, depending on the distance from the core. The radiation spectrum of the sun, when fitted to the black body curve, gives an average temperature of 5800 K. The main difference between the prediction model and the real emission spectra of the sun is in the UV region, which suggests a lower temperature of emission. UV emissions may originate close to the lower chromosphere which has a temperature between 2000 and 4000 K. Above the chromosphere in the corona, the temperature increases to about 1 million K, but, because of a low concentration of gas in this region, the radiation from the chromosphere and the corona amounts to only 0.1% of the total output of solar radiation.

In order to understand temperature uniformity, and thus radiation, one should mention sunspots, which appear in the photosphere. Sunspots can have diameters of 10,000-150,000 km and may last for a few weeks. The radiation in the sunspot area is reduced, due to the suppression of convection heat transfer from the core to the photosphere. Horizontal temperature variations of up to 2000 K are not unusual, but because sunspots occupy only up to 1% of total surface area of the sun, the total solar output is within 0.1% of constant. The distribution of emitted energy is such that 9% is in the UV region, 45% is in the visible range, and the remaining 46% is in the infrared. The above data are based on continuous satellite observations over 10 years. The errors of measurements are in the range of 5-15%, depending on radiation wavelength.

3.2 EFFECT OF ORBITAL VARIATIONS ON ENERGY SUPPLY

The eccentricity of the Earth's orbit causes the distance between the Earth and the sun to change between perihelion (the closest distance) and aphelion (the farthest distance). This causes the radiation received by the Earth, at aphelion, to be 3.5% lower than the average radiation. Moreover, during the last 110,000 years, the Earth's orbit changed from more circular to more elliptical, which produced changes in incident radiation in the order of 10%. The Earth's axis (the line which joins two poles through the Earth's center) is tilted at present at 23.5^{o}. During the last 1 million years, this tilt varied from 22 to 24.5^{o} with a variation period of 41,000 years. The obliquity change affects seasonal variations but does not influence the total radiation intercepted by the Earth.

Finally, due to interaction with other planets, particularly Jupiter, the elliptical orbit is distorted. Full rotation of the ellipse takes 21,000 years and changes the distribution of radiation on the Earth's surface. For example, the perihelion now occurs in January but 11,000-15,000 years from now it will happen in July. This will mean warmer summers and colder winters at that future time.

Solar radiation cannot be measured directly at the sun but can be measured by satellites above the Earth's atmosphere. From these measurements, we know that the

range in radiation flux between perihelion and aphelion is at present in the range of 1411 to 1329 W/m^2. The energy which the Earth intercepts is only a small fraction of the total energy emitted by the sun. Still, the amount of energy intercepted by the Earth in 10 days is equivalent to the total energy derived from the combustion of all fossil fuels available on the Earth or a million times larger than the amount of electrical energy produced in the world in the same period.

3.3 SCATTERING OF SOLAR RADIATION

Two theories give us a fundamental understanding of the phenomenon of light scattering by particles found in the path of the sun's rays as they travel to Earth. The Rayleigh Law defines the conditions of scattering for particles much smaller in diameter than the wavelength of radiation they scatter:

$$I_0 = [9\pi^2V^2(m^2-1)^2(1+\cos\Theta^2)]/2d^2\lambda^4(m^2+2)^2 \qquad [5]$$

where	I_o	intensity of scattered radiation
	V	$= 4\pi r^3/3$
	r	radius of the particle
	m	refractive index
	d	distance
	λ	light wavelength
	Θ	incident ray angle.

This law implies that the scattered intensity increases as the sixth power of particle radius and decreases as the fourth power of wavelength. Therefore, light of shorter-wavelength is scattered more than longer-wavelength light. Gas molecules are atmospheric particles which are much smaller than the wavelength of the sun's radiation thus the Rayleigh Law is followed. Contaminant particles are outside the size criteria and their scattering effect does not follow the Rayleigh Law. Rayleigh scattering is responsible for the blue sky, because blue light is scattered about 10 times more than red light. Scattered light beams are not necessarily lost but rather diverted from their normal course, which also means that they stand a higher chance of being absorbed, since they normally travel longer distances.

Bigger particles, such as clouds, water droplets, and pollutant particles also scatter sunlight based on Mie scattering:

$$I_o = \lambda^2(i_1+i_2)/8\pi^2 d^2 \qquad [6]$$

where I_o intensity of scattered radiation
λ light wavelength
d distance
i_1, i_2 coefficients of the electric and magnetic waves.

Mie scattering is less wavelength dependent, and, in fact, radiation of longer wavelength is preferentially scattered. The effects are slightly more complex because scattering occurs in areas where particles are concentrated causing mainly a multiple scattering. The question, now, is how much of the energy arriving at the top of the Earth's atmosphere is scattered? In a clear atmosphere, the molecules scatter about 6.3% of incident solar radiation back to space. This means that 11.7% of ultraviolet and visible light is scattered, whereas IR radiation is not affected by Rayleigh scattering.

3.4 ABSORPTION OF SOLAR RADIATION

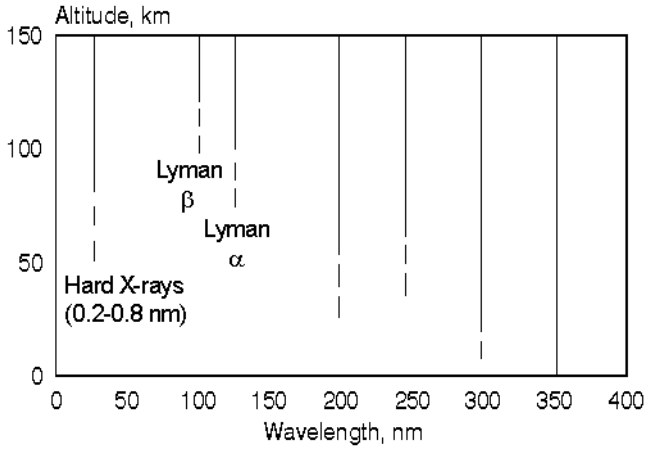

Fig. 3.1. The absorption altitude of incoming solar radiation.

The principles of energy absorption by chemical molecules are outlined in Chapter 1. The effects of energy absorption by molecules contained in the atmosphere are discussed later in this chapter. Here, we deal first with quantitative and qualitative energy loss due to absorption. Fig. 3.1 shows the altitudinal absorption of incoming solar radiation. Two observations can be made: ultraviolet radiation is readily absorbed in the upper layers of the atmosphere; the absorption is wavelength-specific. Therefore, adsorption depends on the composition of the atmosphere in a particular layer. The visible and infrared components of the sun's radiation are not affected by the upper layers of atmosphere. Absorption of infrared occurs in the troposphere, due mainly to clouds and pollutants. Fig 3.2 provides more data on the effect of clouds on radiation transmittance.

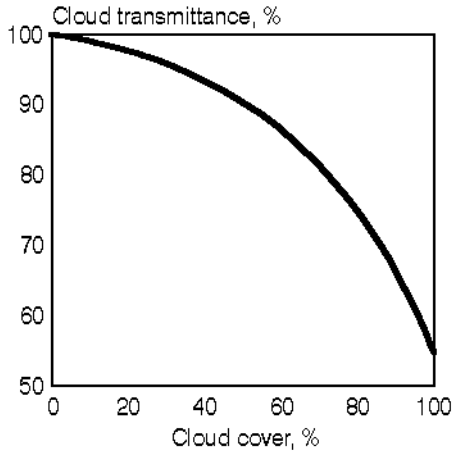

Fig. 3.2. Cloud transmittance vs. cloud cover.

When spectral distribution of incoming solar radiation is compared with outgoing terrestrial radiation, it is evident that the energy absorbed is converted to a higher wavelength (infrared). The shift in radiation wavelength, the negative heat balance at long-wavelength radiation, and, in particular, the energy re-radiation cause the temperature distribution in the troposphere, shown in Fig. 3.3.

Temperature in the troposphere decreases with altitude at a rate of 6.5 K/km. The temperature of the stratosphere increases with altitude at a rate of approximately 2 K/km because of the absorption of short-wavelength radiation. Temperature increase in the thermosphere results from high absorption of energy which causes photo-ionization.

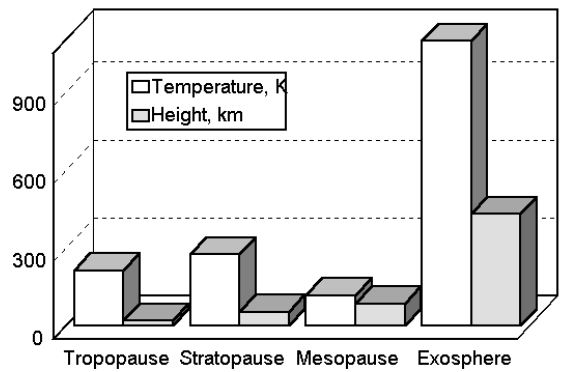

Fig. 3.3. Height in the atmosphere vs. temperature.

3.5 VARIATIONS IN THE RADIATIVE FLUXES

Data on the sun's radiation and its scattering and absorption are summarized in Fig. 3.4. The solar spectrum is modified in both the ultraviolet and the infrared range much more than it is in the visible range. The most important changes occur in the UV range

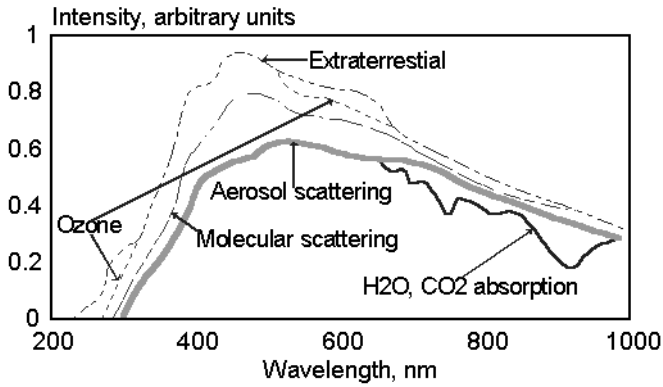

Fig. 3.4. Sunlight spectrum as modified by the presence of various components.

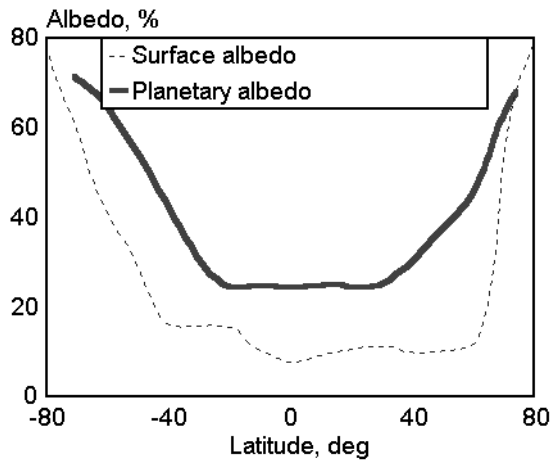

Fig. 3.5. Planetary and surface albedo vs. latitude.

where the ultrashort wavelengths are virtually eliminated. A discussion on radiation intensity is not complete without covering latitudinal, seasonal, geographical, and daily variations in radiative fluxes.

Latitudinal variations in the radiation flux depend on the elevation of the sun, the distribution and type of clouds, and the surface albedo. As the sun's zenith angle increases, the absorption and scattering of radiative energy increases as a result of the longer path it must take through the atmosphere and the higher chance of photon absorption. Fig. 3.2 contains data explaining the reasons for the cloud effect. The surface albedo is the ratio of reflected (scattered) solar radiation to incident solar radiation measured above the atmosphere. Fig. 3.5 presents data on the surface albedo as a function of latitude. The surface albedo of each hemispheres is not the same, due to different cloud distribution. Geographical, seasonal, and daily variations also occur as a result of variations in cloud cover and surface reflectivity as seen from Fig. 3.6.

Snow and ice-cover variations cause the albedo curve in the Northern Hemisphere to reach its maximum in winter. Additionally, one has to consider the effect of the seasonal changes in the sun's zenith angle on the radiative energy supply. If we consider urban climatic conditions and plot the daily radiation flux, we find that the relationship is complicated by an additional parameter - the daily rate of pollution affecting radiation flux by the amount of energy absorbed.

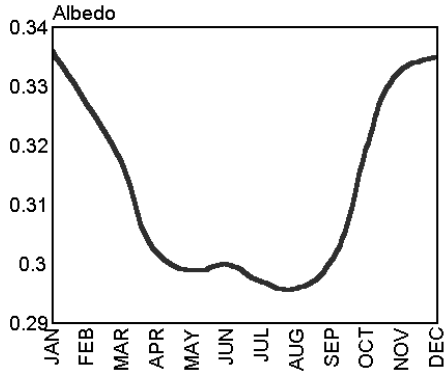

Fig. 3.6. Seasonal variation of albedo.

An effort was made to show what may influence the natural radiation level to which materials are exposed. The value of this data is in the awareness it creates rather than its usefulness as a base material for comparative study. Data clearly indicate that in a natural environment, materials are subjected to a great variety of effects. It is, therefore, essential to develop a data base which characterizes the conditions of degradation if the results of studies are to be used in comparative evaluations.

3.6 TEMPERATURE AND MOISTURE

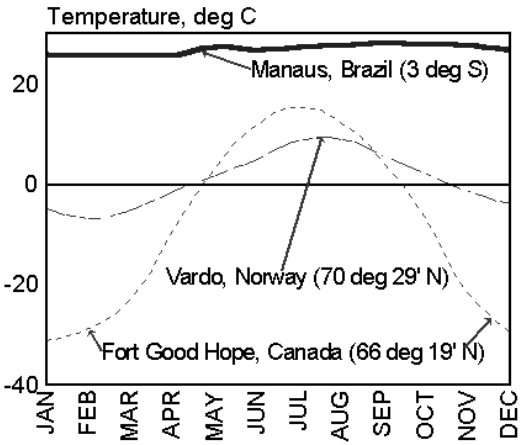

Fig. 3.7. Seasonal temperature variations and latitude.

Seasonal variations of air temperature depend on latitude (Fig. 3.7). Close to the equator, temperatures do not vary much and the radiative flux is uniform. The temperature distribution for Vardo, Norway is characteristic of a coastal location. Large temperature variations occur in a continental interior (Fort Good Hope). The surface temperature of materials is greatly affected by the absorption of radial energy (Fig. 3.8). Material type and color determine surface temperature. The rate of heat penetration depends on the thermal diffusivity of the material, on its heat capacity, and on its thermal conductivity. All three factors together determine surface temperature. Absorption of solar radiation depends on the surface finish. A polished surface reflects more radiation than unpolished surface. Lighter colored materials reflect more than darker. Wind speed has considerable effect on surface temperature increasing the rate of heat exchange.

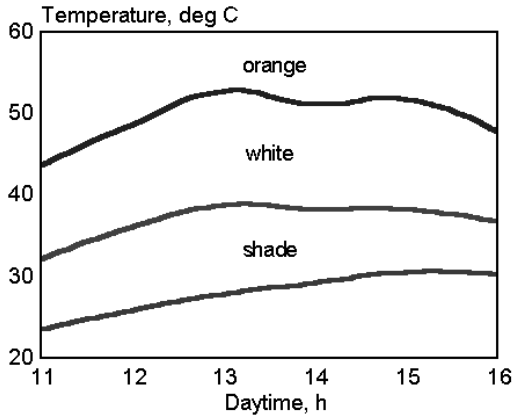

Fig. 3.8. Air temperature behind awning material on sunny days. [Data from E. Hilscher, *Problems with coated polyester fabrics, Ann. Conf. Ind. Text. Group, Text. Inst.*, Manchester, 1975.]

The examples discussed above show that temperature control in weathering studies might be more complex than simple measurement of air temperature. Real temperatures, frequently higher than ambient by as much as 30 degrees, are sufficiently high to have a considerable effect on the degradation rate of many materials.

The atmosphere is the smallest reservoir of water of the Earth, containing only 0.001% of the total water mass. Still, this relatively small amount of water is responsible for scattering and absorption of the sun's energy. Slightly less than one-quarter of the solar influx is used for water evaporation, which is an important regulator of the Earth's temperature.

The molecular weight of water is about 40% lower than the average molecular weight of atmospheric components, which is one of the reasons that a water molecule is very mobile. The average lifetime of a water molecule from evaporation to condensation is about 9 days, which is a sufficient length of time for a water molecule to be carried around the globe by the tropospheric wind system before being precipitated. This explains the considerable latitudinal difference between evaporation and precipitation. Humidity and the amount of precipitation are more local than global climatic phenomena, and, as an important factors in weathering studies, should be carefully monitored.

3.7 ATMOSPHERE COMPOSITION

The total mass of air surrounding the Earth is 5.1×10^{18} kg. Atmospheric density changes exponentially with altitude. About 80-85% of the total atmospheric mass resides in the troposphere, extending from the Earth's surface up to 8-12 km at high latitudes and up to 16 km in the tropics. Most of the water available in the atmosphere is found in the troposphere (the region adjacent to the Earth's surface), which is a region of an active vertical motion due to its negative temperature gradient (almost linear decrease in temperature with increasing altitude). The remaining mass of the atmosphere is found in the next layer the stratosphere. The stratosphere contains about 90% of all atmospheric ozone and controls much of the solar UV radiation reaching the surface and the climate of our planet. The temperature of the stratosphere rises to a maximum at about 50 km due to absorption of UV by oxygen and ozone. The ozone layer has its highest den-

sity at altitudes of 20-25 km. The proportion of nitrogen and oxygen is almost constant up to 100 km. Also, carbon dioxide is fairly evenly distributed throughout the atmosphere, presently at the level of 350 ppm (CO_2 concentration has increased in last 100 years by 70 ppm). Water vapor concentration depends on its saturation vapor pressure and thus, on temperature. It therefore decreases with altitude from about 7% over tropical oceans to 3 ppm in the stratosphere. The mesosphere, thermosphere, and ionosphere, the layers above the stratosphere combined, contain only about 0.1% of the total atmosphere mass.

Gas molecules in the atmosphere are continuously exchanged by the interaction of different sources and sinks. The residence time of molecule in the system is given by the formula:

$$F_i = F_o = A/\tau$$

where
F_i flux of substance into the system
F_o flux of substance out of the system
A amount of substance in the reservoir
τ residence time.

Vertical mixing occurs up to about 50 km and thus occurs faster compared with horizontal mixing (interhemispheric) because the distance from equator to poles is much larger (10,000 km). An exchange of air between the hemispheres takes about a year. This exchange becomes even slower in the stratosphere therefore the southern and the northern stratospheres are practically decoupled.

Based on residence time, the components of the atmosphere were divided into three groups:

quasi-permanent gases	1000 years
variable gases	*a few years*
highly variable gases	*1 year*

This classification is used in grouping the components of the atmosphere, as seen in Table 3.1. Stratospheric composition differs essentially in water and in ozone concentration. Water concentration is on average about 100 times lower and ozone about 100 times higher in the stratosphere than in the troposphere. Ozone concentration in the stratosphere reaches 10 ppm compared to 10-40 ppb at ground level. The similar composition of other components in troposphere and stratosphere suggests that effective exchange mechanisms exist. The tropopause forms a pronounced stability barrier between the troposphere and the stratosphere but it is highly variable in position. Sometimes the tropopause may extend down to 6 km and stratospheric air may be drawn into the tropo-

Table 3.1: Composition of atmosphere

Component	Unit	Concentration	Residence time
Quasi-permanent			
Oxygen	%	20.964	
Nitrogen	%	78.084	
Argon	%	0.934	
Neon	ppm	18.18	
Helium	ppm	5.24	
Krypton	ppm	1.14	
Xenon	ppm	0.087	
Variable			
Carbon dioxide	ppm	330	
Methane	ppm	1.5	9 years
Hydrogen	ppm	0.5	2 years
Nitrous oxide	ppm	0.3	30 years
Highly variable			
Water	ppm	20,000	10 days
Ozone	ppm	0.03	up to 2 months
Carbon monoxide	ppm	0.15	3 months
Nitrogen dioxide	ppm	0.003	1 day
Ammonia	µg	5	5 days
Sulfur dioxide	µg	5	4 days
Hydrogen sulfide	µg	0.5	
Organic carbon	µg	25	less than a day

sphere. In the upper layers of the atmosphere (mesosphere, thermosphere), composition does not differ much except for higher concentrations of elemental hydrogen, helium, and fast oxygen. Except for hydrogen and helium, the components of the atmosphere are relatively constant because they are seldom lost to space.

The components of the atmosphere, which contribute to pollution or interfere with radiative fluxes by participation in photochemical reactions, are discussed below.

3.8 NITROGEN COMPOUNDS

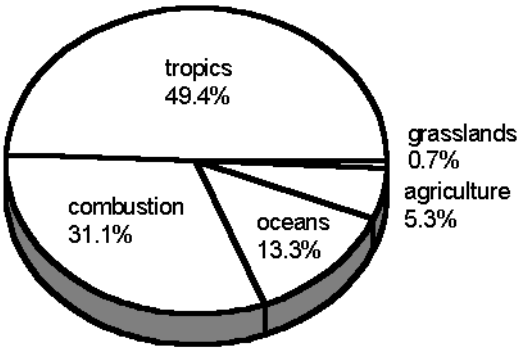

Fig. 3.9. Sources of nitrous oxide.

This group of compounds includes: nitrous oxide, other oxides of nitrogen, and ammonia. Table 3.1 shows their average concentrations and lifetimes. All but nitrous oxide are contained in the group of atmosphere components having highly variable concentrations and short lifetimes. Nitrous oxide has a very long atmospheric lifetime of about 150 years and has very little geographic variation in concentration (<1%). Fig. 3.9 gives information on the sources of nitrous oxide emission, although the presently available data do not account for all nitrous oxide and do not explain its increase. Until recently, combustion, biomass burning, and the use of fertilizers were regarded the most important sources of nitrous oxide. Now, it is known that the influence of biomass burning was overestimated. Currently, the atmospheric concentration of nitrous oxide is 0.31 ppm and growing by 0.3% per year (about 150 years ago it was 0.285 ppm).

The tropical forests produce by far the greatest amount of nitrous oxide followed by world wide combustion of fossil fuels and biomass in the tropics. Nitrous oxide is produced in nature by bacterial denitrification processes which can be decreased by conversion of tropical forest into farmlands and by reducing the use of ammonium salt and urea fertilizers. Nitrous oxide is removed from the atmosphere mainly by photolysis in the stratosphere and by reaction with elemental oxygen:

$$N_2O + h\nu \rightarrow N_2 + O$$

$$N_2O + O\ (^1\Delta) \rightarrow NO + NO \rightarrow N_2 + O_2$$

Presently, its total rate of destruction is about 30% lower than its production and this results in an increase in concentration of nitrous oxide by 0.3% per year. The above reactions show that nitrous oxide, by reacting with elemental oxygen, affects the formation of ozone, the concentration of ozone in the atmosphere, and indirectly, the intensity of UV radiation.

Oxides of nitrogen (NO and NO_2) are decomposed in the atmosphere in a few days and have an important indirect influence on the concentration of tropospheric radicals.

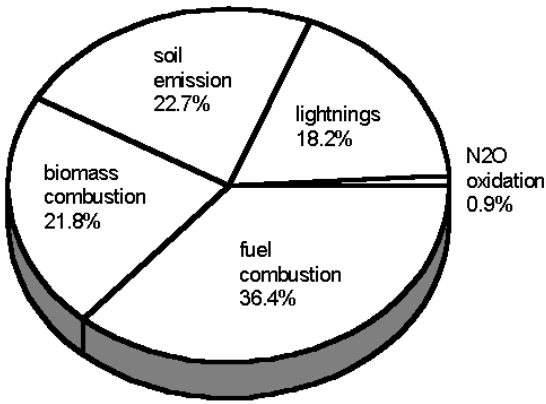

Fig. 3.10. Sources of nitrogen oxides (NO_x).

The short lifetime causes the concentration of nitrogen oxides to be linked geographically to the sources thus the concentration of nitrogen oxides varies in a broad range. Fig. 3.10 shows the sources of nitrogen oxides formation.

Combustion of fuels by vehicle engines, power stations, and industry contribute heavily to the overall emission of nitrogen oxides. In large cities, NO_x is produced by car emission. It is considered that 75% of NO_x emission in Athens, Greece (about 40 kt/year) is automobile emission related. Morning traffic increases the concentration by factor of 3. Nitric oxide is produced from the reaction between molecular nitrogen and oxygen in a lightning flash. The discharge channel may reach a temperature as high as 4000 K. Since there is, on average, about hundred bolts of lightning a second around the globe, the estimated output of nitrogen oxide is not high. The denitrification process in acidic soil also results in the production of nitric oxide, which is then easily oxidized to nitrogen dioxide in the atmosphere. Biomass burning (mostly in tropical countries) produces large quantities of nitrogen oxides steaming from the high nitrogen content of the biomass and the low temperature required for its oxidation.

Nitrogen oxides participate in several chain reactions:

$$NO + O_3 \rightarrow NO_2 + O_2$$

$$NO_2 + O \rightarrow NO + O_2$$

$$NO_2 + O_3 \rightarrow NO_3 + O_2$$

$$NO_3 + h\nu \rightarrow NO + O_2$$

These reactions decrease ozone concentration, reduce the UV filtration barrier in the stratosphere, and contribute to increased UV radiation on the Earth. Additionally, NO_x species interfere with the formation of hydrogen- and chlorine-containing radicals, which, in turn, affects ozone concentration.

The ammonia cycle in the atmosphere is quite simple and short. Its very short lifetime of 2 days is due to its high solubility and reactivity with sulphur-containing compounds. Most ammonia is produced by denitrification with small amounts emitted from coal combustion. Pollution is local, little is oxidized in the troposphere, and most ammonia is returned to the Earth's surface dissolved in water or in the form of ammonium sulphate.

3.9 OXYGEN SPECIES

Oxygen species include atomic (elemental) oxygen, the excited singlet states of molecular oxygen, and ozone. Formation of odd oxygen in the stratosphere and mesosphere starts from the photodissociation of molecular oxygen, which is a two-stage process. Molecular oxygen, on absorption of UV radiation, is transformed into excited singlet oxygen, which dissociates, forming two oxygen atoms. The photodissociation process is followed by a secondary thermal reaction with molecular oxygen in the presence of a neutral body (oxygen or nitrogen) and ozone is produced. Molecular oxygen absorbs solar radiation in the range of 176-210 nm. Ozone has maximum absorption in the range of 280-320 nm.

Ozone decay is also a two-step process. In the first step, ozone absorbs UV radiation and dissociates to molecular and atomic oxygen. Atomic oxygen reacts further with another molecule of ozone and two molecules of molecular oxygen are formed. Ozone absorbs in the UV between 200 and 320 nm and also in the visible range at 450 and 700 nm. Absorbing in the UV range, ozone converts the UV radiation to heat, which causes the stratosphere to have a positive temperature gradient. If the above reactions were the only once occurring, the thermal and radiative balance would be constant. In reality, there are more reactions competing for ozone and atomic oxygen. These have received much public attention since the processes involved could have dramatic effect on life on Earth. It is believed that three reactions have almost equivalent effect on ozone destruction: reaction with NO_x, reaction with chlorine, and recombination with molecular oxygen.

There are two anomalies which may affect the results of weathering studies. One is the drastic increase in ozone concentration at the Earth's surface and the other is the formation of ozone holes. The change in the position of the tropopause causes stratospheric air to be drawn into the troposphere and this causes a major increases in ozone concentration close to the Earth's surface, possibly altering weathering behavior. There are two typical latitudes where such events are more likely to occur: in the proximity of 30^o where air masses of tropical origin meet the colder mid-latitude air and at 60 deg where polar air contacts warmer air. These two latitudes in Northern Hemisphere are known to have higher ozone concentrations. The latitudes between 42 and 45^o, where the tropopause folds between polar and tropical air masses, also have an unusually high ozone concentration. Ozone holes, which form mostly above the poles, can drift to other

locations; these, in turn, may facilitate degradative processes by allowing more UV radiation to reach the Earth.

Two separate processes should be considered in weathering studies. One is related to the above discussed ozone depletion which increases UV radiation. The other is related to the ozone concentration at ground level. Ozone has very short lifetime (about 2 min), therefore the processes of formation and degradation of ozone in the stratosphere are not related to ozone formation at ground level. Similarly, ozone in the stratosphere does not directly contribute to ozone concentration at ground level. Ground level of ozone, because it is so reactive, affects the degradation of materials in its surrounding. Ozone on the Earth surface is produced by industry and transportation. Concentrations are 2-3 times higher in summer than in winter. During the day, peak concentrations follow morning and afternoon peak traffic volumes. Ozone is formed indirectly from nitrous oxide which on absorption of UV forms molecular oxygen which then reacts with molecular oxygen to form ozone. It is therefore not surprising that ozone concentration trails concentration profile of oxides of nitrogen. In Europe, WHO quality guidelines set ozone level at 150-200 $\mu g/m^3$ (1 h average) and 100-120 $\mu g/m^3$ (8 h average). Recorded values in Mexico City are in the range of 300-900 $\mu g/m^3$.

3.10 HYDROGEN SPECIES

The group discussed here includes hydrogen, hydroxyl, hydroperoxyl, peroxide, water, and methane. Hydrogen is not particularly important in weathering studies. It may be appropriate to mention that the concentration of hydrogen is higher in a polluted area because it is a component of automotive exhaust gases (1-5% by volume). Hydrogen is also produced from oceanic sources and soils due to microbiological activities. Altitudinal concentration of hydrogen is constant and it is detected in all layers of the atmosphere. Hydrogen can react with OH radicals, producing water and atomic hydrogen.

Hydroxyl radical generation is mostly due to the reaction between water and atomic oxygen but other pathways are also known:

$$O_3 + h\nu \rightarrow O_2 + O(^1\Delta)$$

$$O(^1\Delta) + H_2O \rightarrow HO^{\cdot} + HO^{\cdot}$$

$$H_2O_2 + h\nu \rightarrow HO^{\cdot} + HO^{\cdot}$$

$$NO + HO_2^{\cdot} \rightarrow NO_2 + HO^{\cdot}$$

Fig. 3.11 shows that the highest OH radical concentration occurs when the sun is at its zenith. These data are in accordance with the photochemical theory of hydroxyl radical formation. The concentration of hydroxyl radical is higher by 28% in winter, than in

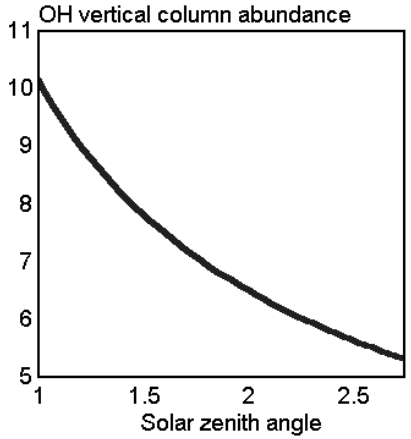

Fig. 3.11. OH vertical column abundance vs. solar zenith angle.

the summer, which is due to seasonal temperature changes. It is difficult to measure hydroxyl radical concentration. Its concentration based on model calculations is 5×10^5 molecules per cm^3. In the tropics, this value is larger by factor of 2. The concentration of hydroxyl radical changes throughout the day and it is at its peak at noon.

The hydroxyl radical concentration is very low because the highly reactive radical has a residence time of less than 1 s. It occupies a special place in atmospheric chemistry because it is reactive to most trace gases. Some of the examples of reactions are given below:

$$CH_4 + HO^{\cdot} \rightarrow CH_3^{\cdot} + H_2O$$

$$CO + HO^{\cdot} \rightarrow CO_2 + H^{\cdot}$$

$$HO^{\cdot} + O \rightarrow O_2 + H^{\cdot}$$

$$CH_3SCH_3 + HO^{\cdot} \rightarrow CH_3SOH + CH_3^{\cdot}$$

$$HO^{\cdot} + H_2S \rightarrow HS^{\cdot} + H_2O$$

$$SO_2 + HO^{\cdot} \rightarrow HSO_3$$

$$NH_3 + HO^{\cdot} \rightarrow NH_2^{\cdot} + H_2O$$

$$NO_2 + HO^{\cdot} \rightarrow HNO_3$$

Accordingly, the hydroxyl radical initiates a chain of oxidation reactions with many components in the atmosphere. The most important reaction concerns the oxidation of methane, which controls the concentration of methane in the atmosphere. Hydroperoxyl radical and hydrogen peroxide both participate in oxidation reactions in a way similar to the hydroxyl radical. Their importance is in balancing the trace components and by indirectly preventing the loss of ozone due to reactions with pollutants.

Methane has had a constant concentration of 0.7 ppm for about 10,000 years (found by testing polar ice). About 150 years ago, its concentration began to rise by 1% per year due to the increase in the area given to agriculture. An increase in methane causes a decrease in the concentration of hydroxyl radical.

3.11 CARBON OXIDES

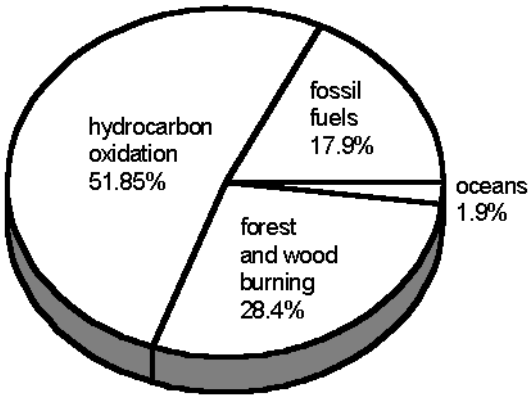

Fig. 3.12. Sources of carbon monoxide.

Carbon monoxide's role in atmospheric chemistry is extremely important because it tends to suppress the atmospheric levels of hydroxyl radicals, leading to longer lifetimes and higher concentrations of methane and the trace components of the atmosphere. Fig. 3.12 gives data on carbon monoxide sources.

Two human activities play a major role in carbon monoxide emission: the use of automotive engines in the Northern Hemisphere and land clearing and savanna burning in the tropics. But both activities produce less carbon monoxide than the oxidation of methane, which is related to natural processes not as much related to human activities. It is estimated that carbon monoxide concentration increases in the Northern Hemisphere by about 1% per year. In the Southern Hemisphere, there is little evidence of increase. Because of its rather short lifetime (2-3 months), carbon monoxide is concentrated close to its emission sites. Its concentration is highly variable (short lifetime) and it is estimated at 0.2 ppm in the Northern Hemisphere and 0.06 ppm in the Southern Hemisphere.

Carbon dioxide is not photochemically active but it is the single most important greenhouse gas in the atmosphere. Because of this, it also has an influence on photochemistry in the stratosphere. Because it is so much related to its uptake by vegetation, the concentration of carbon dioxide is dependent on season and latitude. The Northern Hemisphere has higher concentration because of greater fuel combustion. Sedimentary rocks are the largest reservoir of carbon dioxide. Dissolved calcium and magnesium carbonates are flushed into the oceans by rain, surface and ground water to form new carbonate sediments. A surplus of bicarbonate ion is returned to the atmosphere as carbon dioxide. It is estimated that the concentration of carbon dioxide grows in the Northern Hemisphere by 4% yearly. Other data show that the increase in carbon

dioxide concentration is less than this. Carbon dioxide concentration in 1958 was 315 ppm. By 1988 it has risen to 350 ppm which is an annual growth rate of 0.4%. Doubling the concentration of carbon dioxide in the atmosphere would increase the average temperature by 2.5 K. The process of carbon dioxide removal from the atmosphere takes a long time (lifetime of 250 years or longer) because the amount of carbon dioxide in the atmosphere is large compared to what can be consumed by vegetation. In turn, the excessive removal of carbon dioxide may have adverse consequences as lower concentration would lower the temperature on Earth. Too high a concentration would result in excessive ice melting and an increase of the sea level on Earth. This shows that it is highly desirable to maintain the concentration of all atmospheric components in fine balance.

3.12 SULFUR-CONTAINING COMPONENTS

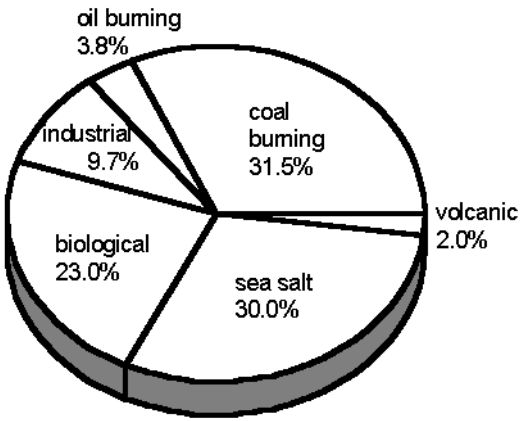

Fig. 3.13. Sources of sulfur-containing compounds.

Several compounds are included in this group: sulfur dioxide, hydrogen sulfide, carbonyl sulfide, and carbon disulfide. Fig. 3.13 presents data on sulfur emission from various sources. Sulfur-containing components of the atmosphere have a short lifetime in the atmosphere - sulfur dioxide 2 days, hydrogen sulfide 0.5 days, carbonyl sulfide more than 1 year, and carbon disulfide, a few weeks. These short lifetimes contribute to local pollution. This agrees with observations of volcanic eruptions which contribute to increases in regional concentration by 20-40%.

Half of all emissions of sulfur dioxide comes from burning of fossil fuels. Other sources include: biomass burning, volcanic eruptions, oxidation of dimethyl sulfide (from the oceans) and oxidation of hydrogen sulfide in the atmosphere. The sulfur dioxide formed is eventually converted to aerosol particles as it combines with water droplets in the clouds. In volcanic eruptions, sulfur dioxide is directly injected into the stratosphere where it has long lifetime. Current theory suggests that aerosols which end up in the troposphere produce a cooling effect in the Northern Hemisphere.

The conversion of original pollutants is explained below:

$$O + CS_2 \rightarrow OCS + S$$

$$OCS + h\nu \rightarrow S + CO$$

$$S + O_2 \rightarrow SO + O$$

$$OCS + O \rightarrow SO + CO$$

$$SO + O_2 \rightarrow SO_2 + O$$

$$H_2S + HO^{\cdot} \rightarrow H_2O\ HS^{\cdot}$$

$$HS^{\cdot} + O_2 \rightarrow HO^{\cdot} + SO$$

$$SO_2 + O \rightarrow SO_3$$

$$SO_3 + H_2O \rightarrow H_2SO_4$$

One look at the products of these reactions shows that the final product will be acid rain. As it is produced, the valuable resource of hydroxyl radicals is consumed. Acid rain and sulfur dioxide are very aggressive, corrosive materials. For example, books and leather bindings deteriorate in library environments because of the presence of these contaminants. Building materials suffer from reactions with sulfur-containing compounds. A typical reaction between sulfuric acid and calcium carbonate produces gypsum which is subsequently washed out. This deterioration process is usually attributed to acid rain but many buildings are in places where pollution is produced therefore reactions may simply occur with gaseous products coming directly from those local sources. This has a high probability given the short lifetime of sulfur dioxide in the atmosphere.

3.13 CHLORINE-CONTAINING COMPONENTS

Chlorinated fluorocarbons have become a subject of particular interest because of their effect on ozone concentration in the atmosphere. Their long lifetime and their direct consumption of ozone pose a threat to the future energy balance. Chlorinated fluorocarbons absorb UV radiation at a wavelength below 300 nm and dissociate to free radicals or react with singlet oxygen, producing more free radicals. Further steps in the chain reaction include ozone, and the reaction cycle may occur hundreds of times before a Cl atom (a product of the primary reaction) is recycled into an inert HCl. This scheme of reactions has been developed after intensive studies of these components. Two compounds are the most common: $CFCl_3$ and CF_2Cl_2. There is 0.28 ppb of $CFCl_3$ in the atmosphere and it has a lifetime of 65 years. The concentration of CF_2Cl_2 is 0.48 ppb and its lifetime is 120

years. Although they do not contain fluorine, carbon tetrachloride and methylene chloride have similar photochemical properties.

Very few studies on hydrogen chloride have been carried out and the results to date are not conclusive. Hydrogen chloride originates from two main sources - photochemical decomposition of other chlorine-containing compounds (mostly methylene chloride) and from volcanic deposition. Other sources include coal burning, incineration (mostly due to the combustion of PVC) and the alkali industry. Hydrogen chloride is widely distributed and present throughout all layers of the atmosphere. It must, therefore, be an important reactive component of the chemical activity in the atmosphere.

3.14 PARTICULATE MATERIALS

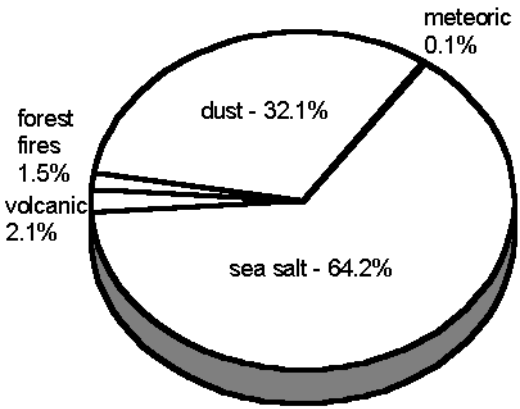

Fig. 3.14. Particles released to the atmosphere.

There are two sources of particulate materials in the atmosphere: particles formed on the Earth's surface and particles formed from chemical reactions in the atmosphere. Global release of particles to the atmosphere is summarized by Fig. 3.14. Forest fires produce small particles (50 nm) with a very high yield of up to several tones per hectare. In tropical areas, land-clearing and savanna-burning continues to be carried out routinely. The largest dust-producing areas include the Sahel, the deserts of Asia, and some parts of the USA. Winds can carry particles to very far; for example, the Harmattan can carry particles from the Sahara desert to England, about 3000 miles away.

Volcanoe eruptions create enormous uplift forces which cause particles to travel great distances because of high ejection velocities. These particles have very large diameters - up to 10,000 nm - and the aerosol is highly concentrated. Sea salt particles are also of relatively large dimensions. These are produced by bubbles of sea breaking into small droplets, which, after evaporation, produce small particles of salt.

Secondary particulate material, formed in the atmosphere, consists of sulfates (mostly ammonium sulfate) and nitrates. The composition of aerosols is usually determined by local conditions, but particles need not have a simple composition related to their source of origin. For example, elements such as mercury, cadmium, and selenium are found in atmospheric particulates in concentrations much higher than are found in

seawater. This shows that particles undergo an enrichment process which changes their composition. Such processes may include the volatilization of metals through methylation, deposition of surface-active organic species, and biological processes which modify the aerosol composition. Finally, gas molecules may be absorbed followed by thermal and photochemical reactions. Many of these processes may continue to be active at high altitudes.

Deposition of suspended particles depends on their size. Particles having diameter 20 μm can be easily lifted into the troposphere and can be transported over large distances. Their lifetime can be very long (1 year and more). Smaller particles have almost infinite lifetimes. Larger particles fall back with a rate which increases exponentially with their weight and diameter. The mass of all particles returning to the Earth's surface is estimated to be 4 g/m^2 year. Particulate materials have two effects on the weathering process of materials: they can be deposited on the sample surface (most likely by impaction) and also they absorb part of radiant energy from sun. The absorption is more pronounced in the UV and visible regions than in the infrared.

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